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| 13. ABSTRACT (Maximum 200 words) THE OBJECTIVE OF THIS REPORT IS TO OUTLINE A PRELIMINARY PLAN FOR MONITORING GROUND WATER, SOIL, VEGETATION, AND AIR IN THE VICINITY OF THE HYDRAZINE BLENDING AND STORAGE FACILITY (HBSF). THE ANALYTES OF INTEREST ARE HYDRAZINE, UDMH AND NDMA. METHODS FOR CHEMICAL ANALYSIS OF THE ABOVE FOUR MEDIA ARE DISCUSSED. RESULTS OF PRELIMINARY SAMPLING OF AIR AND SOIL ARE INCLUDED, AS ARE SMALL MAPS SHOWING THE LOCATION OF WELLS AND SAMPLING POINTS. | | | | | |
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ROCKY MOUNTAIN ARSENAL
PRELIMINARY
MONITORING PLAN
FOR
HYDRAZINE BLENDING FACILITY
PRELIMINARY REPORT

1. PURPOSE. To report on the status of the "Preliminary Monitoring Plan For Hydrazine Blending Facility" as revised and submitted on 7 July 1983 and approved for action in October 1983.

2. OBJECTIVES. To outline a preliminary plan for monitoring groundwater, soil and vegetation in the vicinity of the Rocky Mountain Arsenal (RMA) hydrazine blending facility. Analytes of interest are hydrazine (H₂), unsymmetrical dimethylhydrazine (UDMH) and N,N'-dimethylnitrosamine (NDMA). The analytical results will be used to develop a first approximation of the degree of contamination present in specific areas of the facility.

3. HISTORICAL. The Rocky Mountain Arsenal hydrazine blending facility was constructed in 1961 for blending H₂ and UDMH to make Aerozine 50. Aerozine 50 is used primarily by the U S Air Force (USAF) as a rocket fuel.

An incident occurred in November 1973 when the fire protection system malfunctioned due to a power outage. Several hundred thousand gallons of water filled the pit around the large (200,000 gal) UDMH storage tank causing it to float. The water from the pit area was pumped onto the fields to the east and south of the east yard (Figure 1). In May 1976 approximately 4 inches of UDMH was found in the pit around the large tank due to leaks in the tank. The UDMH was pumped to the sump (B-739) and was neutralized.

During the productive years many of the drums returned for filling contained residues of up to several gallons. These residues were poured into the sump to be neutralized. The drums were then washed in the open area south and east of building 733 (Figure 1).

In 1991 RMA requested the U S Occupational Safety and Health Agency (OSHA) to make a survey of the hydrazine facility to determine compliance with existing regulations and the safety of the working environment. Measurable levels of NDMA were found. NDMA, a degradation product of UDMH, is a carcinogen. The facility was shut down and remains in a storage-caretaker status at this time.

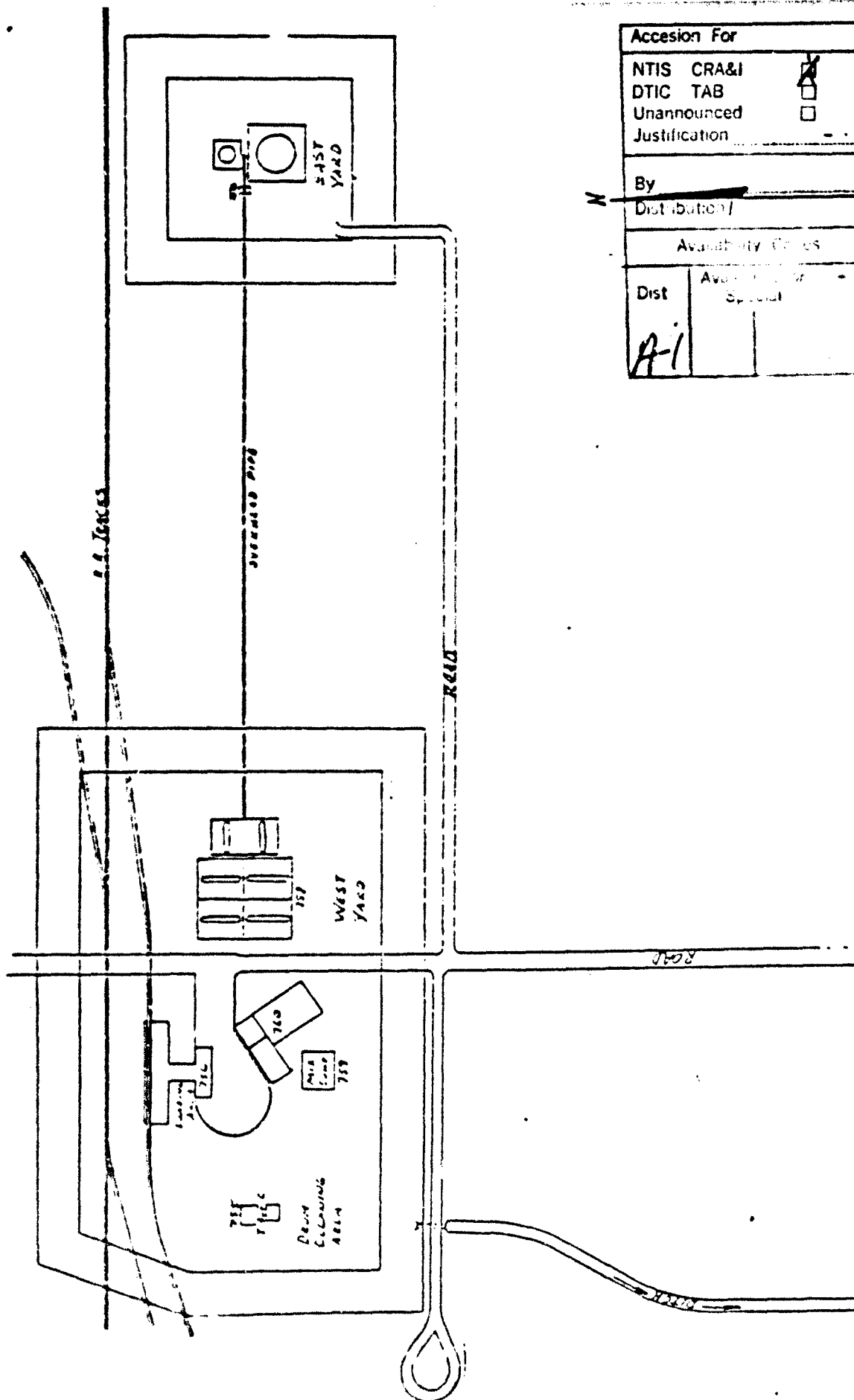


Figure 1. Layout of hydrazine facility.

4. METHODS:

a. Air. Air samples were taken at 3 feet above ground level. Ambient air was taken through glass tubes packed with Thermo Sorb-N at the rate of 1.0 liters per minute (1L/min) for two hours. The sample tubes were extracted with solvents, the solvents concentrated and analyzed by gas chromatography (GC) using a Nitrogen/Phosphorous detector.

The first round of sampling following the OSHA report was done by the Army Environmental Hygiene Agency (AEHA). Sampling sites were established as indicated in Figure 2. Selected sites from that study were used in three subsequent rounds of sampling by RMA personnel.

In the initial RMA sampling round duplicate samples were taken at each site sampled. One set of samples were sent to the Thermal Electron Corporation for analysis. The other set was analyzed at RMA by the Analytical Systems Branch (ASB) laboratories. The second and third rounds of samples were analyzed only by the RMA-ASB laboratories. These three rounds of sampling were undertaken in an effort to locate and repair leaks in the UDMH and Aerozine 50 piping systems and other hardware. For this reason sample sites were added or deleted in each successive round as deemed necessary.

b. Soils. A lack of methods for analysis of soils for H₂, UDMH and NDMA resulted in assigning a Reserve Chemical Officer Major John Neil the task of compiling a list of work done in this field. Major Neil contacted personnel in the USAF, OSHA, EPA and possibly other agencies. His efforts resulted in receipt of some ten papers on H₂, UDMH and/or NDMA analysis. Six papers indicated work had been done with varying degrees of success on one or more of the three compounds of interest in soils. Only two methods, Colorimetry and Gas Chromatography (GC) or tandem coupled Gas Chromatography/Mass Spectrometry (GC/MS) were described. The GC and GC/MS methods both used Thermal Energy Analysis (TEA) equipment in the isolation and analysis of the analytes. The lack of TEA equipment at RMA-ASB has necessitated the development of an extraction and analysis procedure for soils based on the formation of stable derivatives.

A method of determining the areal distribution of components in soil atmosphere has been developed by Dr. Kent Voorhees and his associates at the Colorado School of Mines, Golden, Co. The method consists of excavating a hole in the soil approximately 8 inches deep. A four inch long curie point wire tipped with an adsorbent is placed upright in the hole and covered with a 12 oz capacity aluminum can. The can is then covered with soil and left for a specified period of time. After the specified time the

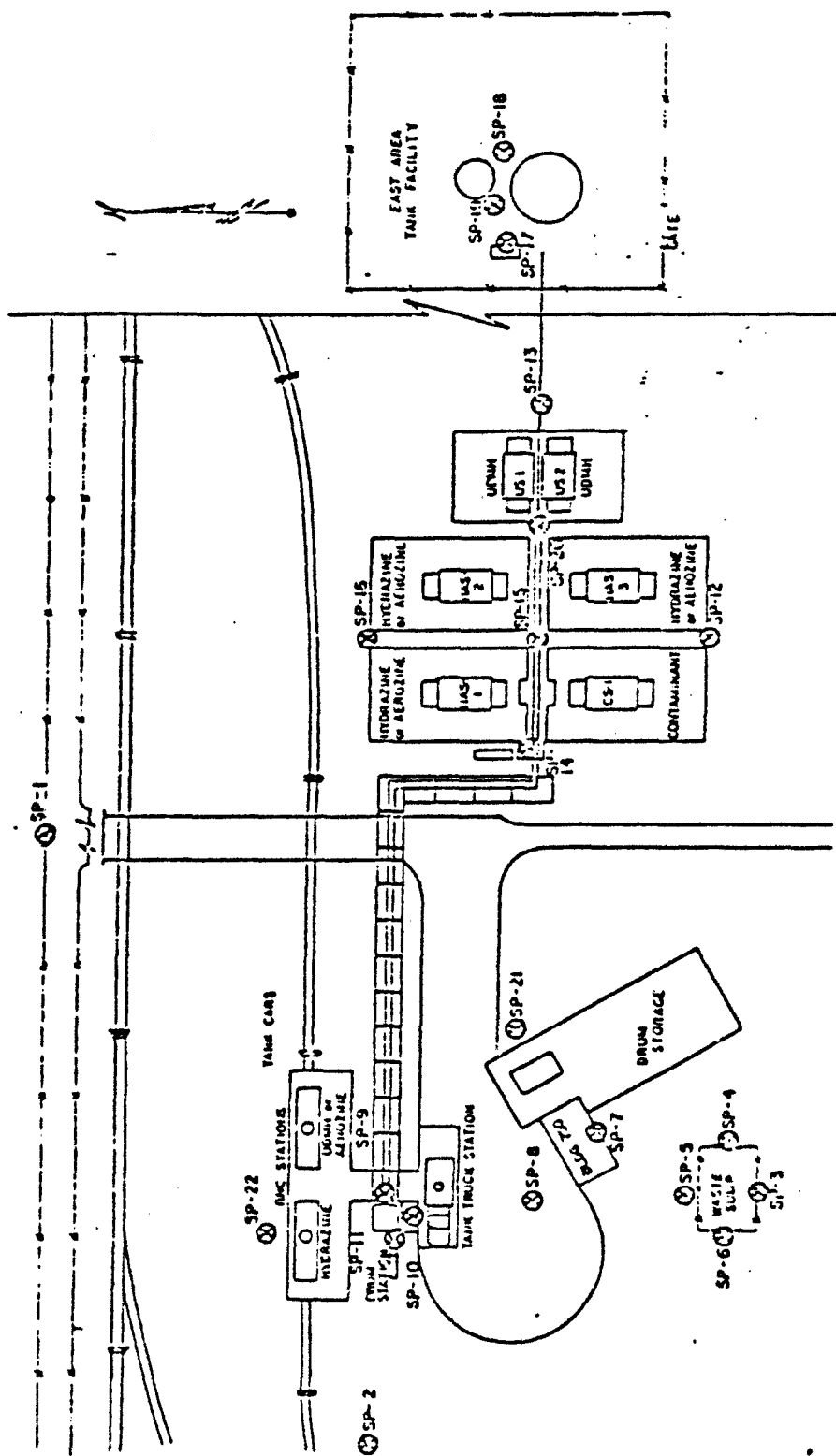


Figure 2. Location of air sampling sites as set by AEHA.

wires are recovered and analyzed on tandem coupled mass spectrometers with a data system (MS/MS/DS). Due to the low cost of this method it was decided to do a preliminary study of the facility to determine the most appropriate positions for taking soils samples for analysis.

c. Water. Analysis of water samples are being done by the derivative method developed at RMA. The three methods of water analysis reported in the collected literature relied upon Colorimetric or TEA-GC analysis. Equipment for TEA analysis is not presently available at RMA-ASB laboratory.

d. Vegetation. There is very little published material dealing with the analysis of H₂, UDMH and NDMA in plant tissue. One reference was found which mentioned the analysis of plant tissues for UDMH. The RMA-ASB laboratory will attempt to adapt its derivative-GC method for use with plant tissue.

5. RESULTS:

a. Air. After the AEHA reported concentrations of H₂, UDMH and NDMA in the air at the hydrazine facility in 1982, it was assumed that the H₂, UDMH and NDMA were originating from the leaks in the plant pipes. A monitoring program was begun to attempt to locate any leaks which could then be repaired. Figure 2 shows the sampling sites. After each sampling period sites were added or deleted in an attempt to better pinpoint sources of contamination.

The air sampling was accomplished by personnel from the ASB and the Hydrazine Facility operators under the direction of Messrs. Elijah Jones, Dave Strang, Tom James and Martin Macias.

The results of the three rounds of samples collected by RMA personnel are presented in Table 1. Repairs of the facilities were made between sampling rounds but little total progress is indicated.

b. Soils. Due to the amounts of H₂ and UDMH reported to have been distributed on the ground because of incidents and "state of the art" cleaning, mixing and filling procedures, it was deemed prudent to conduct a small soil gas survey to determine the locations at which to take soil samples.

Sixteen wires were set out in and around the Hydrazine Facility (Figure 3). The wires were allowed to remain in place for seven days and were then recovered and analyzed. The results (Table 2) are given in total ion counts at mass to charge ratio (M/Z) 28 the molecular weight of nitrogen. These ion counts are compared to a background ion count at M/Z 28 of 105. The background ion count of 105 was based on other work of this kind done previously in

| Site No. | Date Taken (1983) | TEC Lab NDMA (ug/m ³) | ASB Lab NDMA (ug/m ³) | Date Taken (1983) | ASB Lab NDMA (ug/m ³) | Date Taken (1983) | ASB Lab NDMA (ug/m ³) |
|-------------|-------------------------|--------------------------------------------|--------------------------------------------|-------------------------|--------------------------------------------|-------------------------|--------------------------------------------|
| 1 | | | | 22 Feb | 0.55 | | |
| 2 | | | | 22 Feb | 0.38 | | |
| 3 | | | | 28 Feb | 0.25 | 12 Apr | ND |
| 4 | | | | 28 Feb | 0.35 | | |
| 5 | 14 Jan | ND | ND | 28 Feb | Trace | 12 Apr | Trace |
| 6 | | | | 28 Feb | 0.33 | | |
| 7 | 14 Jan | ND | ND | 28 Feb | 1.43 | 11 Apr | 0.72 |
| 8 | 14 Jan | ND | ND | 28 Feb | 2.57 | 11 Apr | 0.37 |
| 9 | 13 Jan | 5.20 | 5.27 | 22 Feb | 3.27 | 8 Apr | 9.30 |
| 10 | 13 Jan | 0.26 | 0.39 | 22 Feb | 0.88 | 8 Apr | 8.01 |
| 11 | 13 Jan | ND | ND | 22 Feb | 2.44 | 8 Apr | 62.51 |
| 12 | 14 Jan | ND | ND | | | 11 Apr | 0.51 |
| 13 | 14 Jan | ND | ND | | | 11 Apr | ND |
| 14 | 14 Jan | 0.41 | 1.10 | 28 Feb | 2.38 | 11 Apr | 2.22 |
| 15 | | | | | | 11 Apr | 0.94 |
| 16 | | | | | | 11 Apr | 0.47 |
| 17 | | | | | | 12 Apr | ND |
| 18 | | | | | | 12 Apr | ND |
| 19 | | | | | | | |
| 20 | 14 Jan | 0.22 | 0.35 | | | | |
| 21 | | | | | | | |
| 22 | 13 Jan | 0.49 | 0.75 | 22 Feb | 8.78 | | |
| 23 | 13 Jan | 0.14 | 0.27 | 22 Feb | 7.41 | 8 Apr | 3.63 |
| 24 | | | | 22 Feb | 12.87 | 8 Apr | 6.78 |
| 25 | | | | 22 Feb | 2.60 | 8 Apr | 16.20 |
| 26 | | | | 22 Feb | 0.68 | | |
| 27 | | | | 28 Feb | 0.32 | | |

Trace = 0.05-0.15
ND = <0.05

Trace = 0.07-0.15
ND = <0.07

Trace = 0.07-0.15
ND = <0.07

TABLE 1

Results of air monitoring
at the RMA hydrazine facility

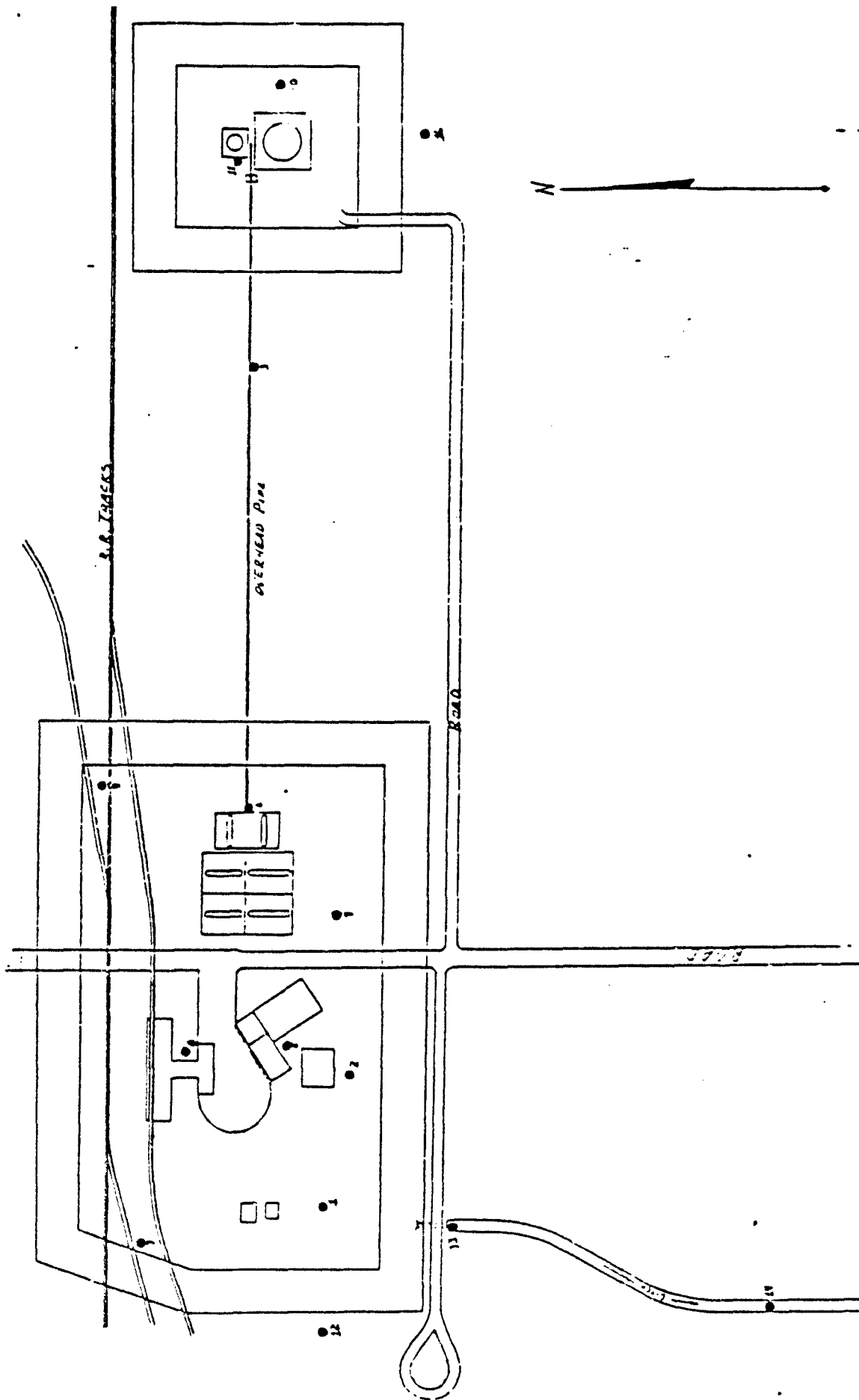


Figure 3. Locations of 16 soil gas samples.

| <u>Site No.</u> | <u>Ion Counts</u> | <u>Background Multiple</u> |
|---------------------|-----------------------|--------------------------------|
| 1 | 3114 | 23.06 |
| 2 | 2604 | 19.29 |
| 3 | 2924 | 21.66 |
| 4 | 2089 | 15.47 |
| 5 | 2639 | 19.55 |
| 6 | 1254 | 9.29 |
| 7 | 1953 | 14.47 |
| 8 | 3334 | 24.70 |
| 9 | 2446 | 18.12 |
| 10 | 2690 | 19.93 |
| 11 | 1965 | 14.56 |
| 12 | 1759 | 13.03 |
| 13 | 2919 | 21.62 |
| 14 | 2015 | 14.93 |
| 15 | 2420 | 17.93 |
| 16 | 832 | 6.16 |

TABLE 2

Total ion counts at M/Z 28 and multiples of background level
as determined by the soil gas method

other areas of the RMA.

The ion counts are contoured on Figure 4. The contour lines indicate the trend of concentrations of nitrogen (N) and nitrogen containing compounds in the soil and/or underlying ground water. The highest concentration of 3334 counts is approximately 25 times RMA background. This was found at the drum and tank car loading facility (site 9). The second highest concentration of 3114 counts is 23 times background. This was located at site 1, just south of building 755 where the drum cleaning was done. Figure 4 indicates the contamination components follow surface drainage patterns with subsequent infiltration.

One set of soil samples were taken at site 13, outside the facility fence. These samples were used to determine the effectiveness of the first soil extract and furfural derivative method. The derivatives lacked the desired stability and other derivatizing agents were tried. Presently a derivative method is being developed at the ASB by Mr Glen Kalas DAC, which seems to form more stable azine and hydrazine derivatives.

The remainder of the soil samples from inside the facility fences have not yet been taken as stability of the analytes is not good once the soils are aerated in the collection process and before stable derivatives are formed. Since the hydrazine facility operators also work in the laundry, access to the facility is very limited until the laundry passes its Security Operations Inspection (SOI).

c. VEGETATION. The approval of the sampling plan in October '83 made it necessary to wait until the spring of '84 to collect useable vegetation samples. Due to the nature of the analytes sought the greatest chance of success will lie with collection of new growth.

The derivative method of analysis being developed at the ASB for Hx and UDMH should also work with the plant extracts. The extraction of the analytes from the plant tissue may require additional work since there is very little published material pertaining to the extraction of Hx, UDMH and NDMA from plant tissue.

d. WATER. A number of wells in the hydrazine facility area have shown the presence of high levels of nitrates of up to 2 PPM in the water. Unfortunately most of these wells were not analyzed regularly for nitrates. The wells closest to the hydrazine facility, wells 1-008, 1-019, 1-020 and 1-022 were not previously analyzed for nitrates. These wells (Figure 5) are now on the sampling schedule and will add to a more complete picture of the contamination in the facility area.

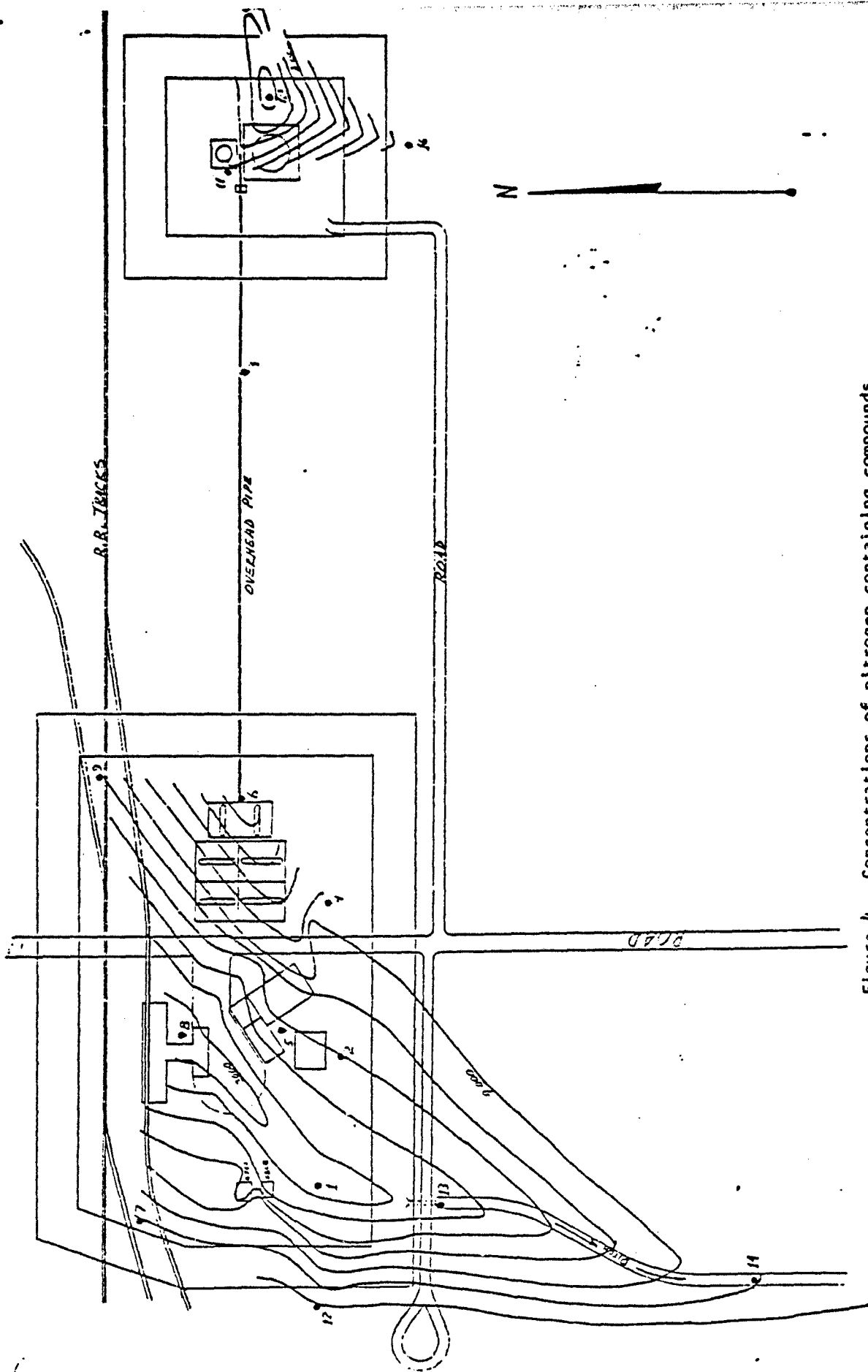


Figure 4. Concentrations of nitrogen containing compounds in soil gas in and around the hydrazine facility.

6. CONCLUSIONS. The curie point wire method of soil gas analysis seems to hold great promise as a tool to determine the areal extent of soil and ground water contamination. The method is swift and relatively inexpensive. Use of this method in preliminary work can result in a better understanding of the problem at hand and a more useful sampling or drilling plan.

There has been some work done by other laboratories and researchers on the extraction and analysis of H₂, UDMH and NDMA from soils and vegetation. Most of this work was done in the laboratory on samples soaked with the analytes and extracted almost immediately or under conditions which do not relate to field samples. All of this is very necessary background for development of useable methods. However very little has been published on the successful extraction of soil and vegetation field samples.

The presence of high nitrate levels in ground water has been noted at various distances and directions surrounding the hydrazine facility. A more organized monitoring program should be instituted using both existing and additional wells. Analysis for nitrates/nitrites and organic nitrogenous entities should be done on wells in this area on a regular schedule.

The history of the hydrazine facility indicates possible additions of H₂ and UDMH to the soil through spills and during drum cleaning. The soil gas study verified the presence of elevated amounts of nitrogenous compounds in the soil and indicated trends in location. An expanded soil gas investigation should be conducted to include the area surrounding the hydrazine facility.

The ground water samples will be retaken to allow use of the salicylaldehyde derivative method of analysis. Useable vegetation samples cannot be harvested until adequate growth occurs in the April-June time frame. The remaining 10 soil samples (5 sites x 2 depths) will be taken as access to the facility is allowed and laboratory assets are available. This is expected to be within the next few weeks.

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